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Biased Deposition of Nanocrystalline $Be_{1-x}Cu_x$ Coatings

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Biased Deposition of Nanocrystalline $Be_{1-x}Cu_x$ Coatings

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ABSTRACT

Coatings of $Be_{1-x}Cu_x$ are prepared by magnetron sputter deposition onto spherical polymer mandrels. The application of an applied bias during deposition refines the columnar morphology of the coating and surface finish to the nanoscale. A mechanical testing technique is developed to load the thin-walled spherical capsules under uniaxial tension at constant strain to fracture. The bias-deposited material exhibits an increase in strength by a factor of three or more following a Hall-Petch type relationship with surface roughness.

INTRODUCTION

The properties of sputter deposited coatings are sensitive to growth morphology and microstructure. The variation of deposition conditions will often effect the formation of the deposited coating. The application of a bias potential applied to the substrate can promote a dense crystalline microstructure through ion bombardment which minimizes porosity and can increase the mechanical strength of the coating.

A promising, inertial confinement fusion target design is a uniformly thick, Be-based fuel capsule.[1] A specific alloy system of interest is $Be_{1-x}Cu_x$ as it offers the potential for improved performance as an ablating material since it has lower opacity, a larger ablation rate, more initial mass, and higher bulk strength than many polymeric counterparts. The performance advantages for Be capsules are accompanied by demanding material requirements. The design criteria include a surface finish of less than 2 nm rms roughness, hence the microscopic control of both structure and concentration. A coarsening of textured crystalline growth produces roughness in the capsule surface that sequentially leads to Rayleigh-Taylor instability during the ablation, a degradation in compression, and cooling of the fuel. Therefore, it's advantageous if the deposition process can accommodate an in-situ smoothing of the surface. In addition, the need to fill and store (at room temperature) a high pressure gas is facilitated by mechanical strength.

The refinement of grain size to the nanoscale is potentially optimal to smooth the coating surface and increase the material strength. It is widely known from prior studies of evaporation and sputter deposition that the grain size of nominally pure beryllium can be dramatically refined through the incorporation of impurities as transition or refractory metals.[2-5] A complimentary evaluation is provided in this report of the changes in growth morphology and strength found for the biased deposition of Be-rich coatings.

EXPERIMENTALS

The samples are prepared by combining sputter deposition with vibration levitation as described in detail elsewhere.[6] The deposition chamber for this study contains a circular array of three 3.3 cm diameter planar magnetrons. Two of the magnetron sources are used to sputter nominally pure Be and the third a $Be_{0.94}Cu_{0.06}$ target blend. The center of each magnetron source is located along the circumference of a 7 cm diameter circle at a 120° separation. The deposition chamber is cryogenically pumped to a 5×10^{-6} Pa base pressure. A 0.4 Pa sputter gas pressure is maintained using a 30 $cm^3\,min^{-1}$ flow of Ar. The nominal deposition rate from each sputter target is 0.2 nm $W^{-1}\,min^{-1}$. The substrates are spherical capsules of a (CH) polymer with a wall thickness of 12-15 μm and an outside diameter of 1 mm. The substrates are levitated 6 cm beneath the center of the magnetron source array. A bowl-shaped substrate pan is driven with an ultrasonic pulse that causes the spheres to randomly bounce and produce a uniformly thick coating. A negative bias potential applied to the substrate pan provides the condition for the ionized Ar sputter gas to collide with the coating surface during the deposition process.

The composition of the alloy is determined from calibrated deposition rates and confirmed through measurements of coating thickness (t) using a contact profilometer and as measured using an electron microprobe. The roughness of the capsule coating is determined through the use of a sphere mapper, i.e. an atomic-force microscope (AFM).[7-8] The root-mean-square (rms) measure of roughness is directly computed from the topological surface profile.

The capsule strength is measured by uniaxially loading a 1 mm diameter hollow sphere in tension. To accomplish this objective the capsule is bonded, through the use of a high strength epoxy, between the ends of two concentrically aligned stainless steel tubes of an appropriate 0.76 mm (i.e. 30 mil) inner diameter. The free ends of the steel tubes are apriori fed through uniaxially aligned sleeves that are pin-mounted into the universal C-clamps of the tensile tester. A 5 N (i.e. 1.1 lb) load cell applies the tensile load (P) at a constant strain rate of 0.5 mm min^{-1}. The tensile load is monitored as a function of crosshead displacement. The stress normal to the shell cross-section is equal to $P \bullet A^{-1}$ where the area (A) equals $\pi\ (r_o^{\ 2} - r_i^{\ 2})$ and r_o, r_i represent the inner and outer radii, respectively. An equivalent rupture pressure (p) equaling $2\sigma_f \bullet t \bullet r_o^{\ -1}$ can be computed at the fracture stress (σ_f).

RESULTS

The physical properties of $Be_{1-x}Cu_x$ coatings are sensitive to the growth morphology and microstructure of the sputter deposit. The application of an applied bias to the substrate can increase the density of the columnar microstructure of a crystalline coating through ion bombardment and smooth the surface by milling. The effect of bias on the $Be_{1-x}Cu_x$ coating is a minimization of porosity, increased mechanical strength, and a reduction of surface roughness. Detailed results and the limitations to each improvement will be quantified for the specific case of 7-11 µm thick $Be_{0.98}Cu_{0.02}$ coatings.

Morphology and Surface Finish

The use of AFM to characterize $Be_{1-x}Cu_x$ coatings provides a useful measurement of the surface finish. Two typical examples are seen in the AFM patch scans (of Fig. 1) for 10 µm thick, sputter deposited $Be_{0.98}Cu_{0.02}$ coatings.[7] The application of bias refines the columnar size and concurrently reduces the rms surface roughness from 0.15 µm for the condition of no bias (Fig. 1a) to only 40 nm for a -120 V bias (Fig. 1b) in these samples. The variation of surface finish with the $Be_{1-x}Cu_x$ coating thickness (for x less than 0.03) is plotted (Fig. 2) with the applied bias voltage. In general, a progressive decrease in surface roughness occurs with an increase in coating thickness and applied bias. The apparent lower plateau in rms roughness seen at 40 nm for the -80 V bias condition (Fig. 2) makes it uncertain whether further improvement in surface finish can be obtained for $Be_{0.98}Cu_{0.02}$ coatings greater than 0.1 mm in thickness.

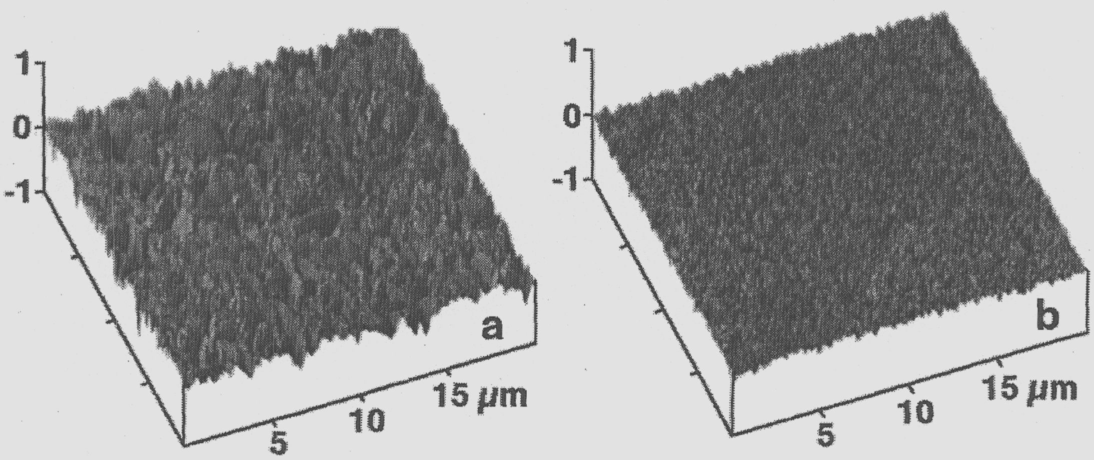

Figure 1. Atomic force microscope images of 10 µm thick, $Be_{1-x}Cu_x$ coatings as sputter deposited (a) without an applied bias and (b) with a -120 V applied bias.

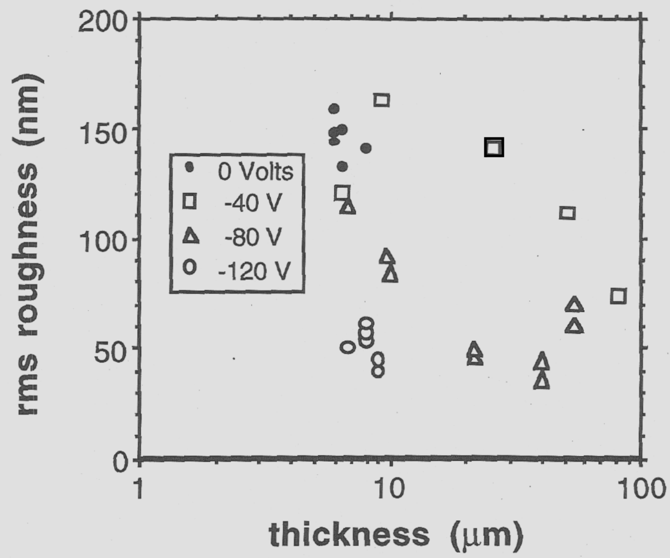

Figure 2. The variation of rms surface roughness with the thickness of $Be_{1-x}Cu_x$ coatings sputter deposited on capsules as a function of applied bias voltage.

<u>Mechanical Properties</u>

The $Be_{1-x}Cu_x$ coated, spherical capsules are loaded under uniaxial tension to failure at a constant strain rate. The halves to a fractured capsule (Fig. 3a) and a higher magnification image in cross-section (Fig. 3b) are seen in the optical microscope images of a 25 µm thick coating on a 15 µm thick, 1 mm diameter mandrel. The following criteria is adopted to enable a comparative analysis of the bias effect on load data. The fracture of the capsule must occur near its equator. Otherwise, the cross-section can't be assumed to have failed in tension. For example, the high magnification view (Fig. 3b) shows a continuous topology to the 25 µm thick, coating cross-section confirming that initial fracture propagates from the capsule surface through the mandrel.

The effect of a -120 V substrate bias on increasing the material strength is seen in the load versus displacement curves (of Fig. 4). The applied bias voltage increases the tensile load of a 10 µm thick coating to a value of 6.9 N (extrapolated) at failure in comparison to the 0.8 N load measured for a 7 µm thick coated capsule deposited without a substrate bias. For reference in computing the $Be_{1-x}Cu_x$ coating strength, the uncoated (CH) polymer mandrel fails at 0.2 N. The mandrel strength equivalence is only 6 MPa.

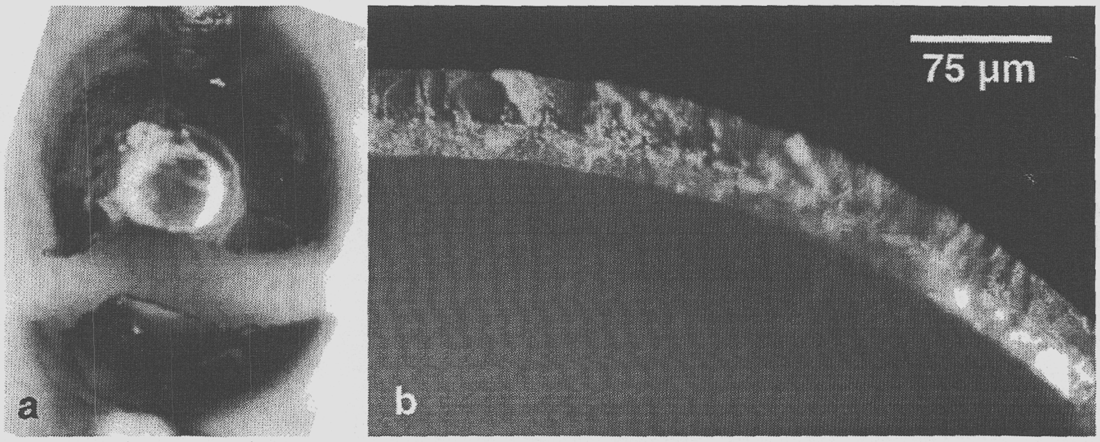

Figure 3. The optical microscope images of the (a) 1 mm dia. $Be_{1-x}Cu_x$ coated capsule tested to failure and (b) fracture cross-section at higher magnification.

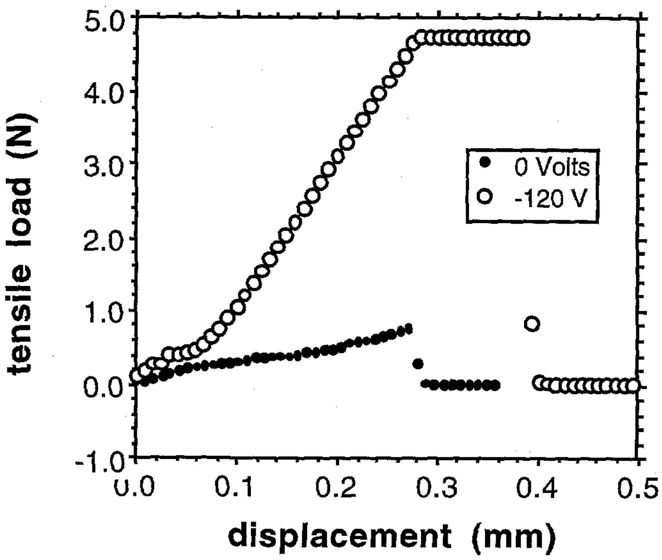

Figure 4. The load versus displacement variation of coated capsules tested to failure under tension as deposited with (a -120 V) and without (a 0 V) substrate bias.

ANALYSIS

The surface roughness measurements for the 7-10 μm thick coatings are listed in Table 1 as a function of applied bias voltage. Only a few of the 7-10 μm thick, $Be_{0.98}Cu_{0.02}$ coated capsules are available for tensile testing. The average strength for those coatings that failed at or near the capsule equator are computed and listed in Table 1. The results for the applied bias conditions of 0 V and -40 V are combined in order to analyze the relationship between surface finish and strength. This rationale is applied for a meaningful quantitative analysis since (a) only one -40 V bias deposited sample, tensile test result is available, and (b) the values for roughness are statistically indistinguishable for the 7-10 μm thick coatings deposited at 0 V and -40 V bias. A plot (Fig. 5) of the fracture stress, i.e. strength, versus the square root of reciprocal surface roughness yields a linear relationship (with a correlation coefficient of 0.978). This behavior is analogous to the well known Hall-Petch relationship for yield stress with grain size. A limitation of the epoxy strength did not permit the testing to failure of very thick coatings. For example, a 77 μm thick coating deposited at a -80 V applied bias did not rupture in the capsule but failed within the epoxy joint indicating a coating strength that exceeds 40 MPa (5.7 ksi).

Table I. - Properties of Bias-Deposited $Be_{0.98}Cu_{0.02}$ Coatings

bias potential (V)	surface rms (nm)	strength (MPa)
0	145 ± 8	25 ± 3
-40	176 ± 62	52
-80	97 ± 16	89 ± 11
-120	49 ± 8	148 ± 49

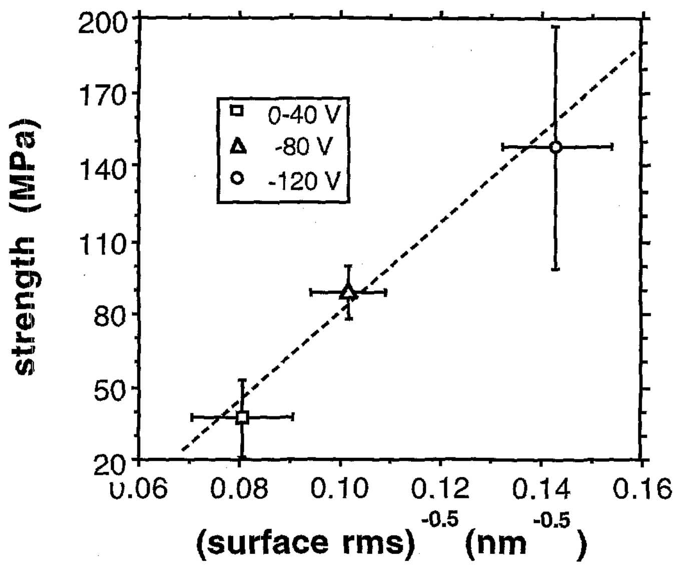

Figure 5. The strength linearly varies with the square root of reciprocal surface roughness for 7-10 μm thick bias deposited, $Be_{0.98}Cu_{0.02}$ coatings.

In order for a 0.150 mm thick, $Be_{1-x}Cu_x$ coating deposited on a 2 mm diameter capsule to hold a gaseous-fill (p) of 300 atm (4.4 ksi) at room temperature [7], the material strength (σ_f) must exceed 119 MPa (17 ksi). The application of substrate bias can produce a $Be_{0.98}Cu_{0.02}$ coating with a failure strength that routinely reaches this value. Through the use of cryogenic cooling, the effective gas pressure is reduced and the strength requirement relaxed considerably.

DISCUSSION

Improvements in the material strength and surface finish of $Be_{1-x}Cu_x$ coatings result from an applied substrate bias. However, it appears necessary to develop alternatives to the $Be_{1-x}Cu_x$ alloy in order to achieve a surface finish with less than 2 nm rms roughness. As one alternative, the use of B in substitution for Be forms a binary system that is a potential metallic glass former.[9] Surface roughness values dramatically decrease to less than 3 nm rms for B concentrations above 11 at.%.[8] However, the decrease in roughness found for the 5 μm thick $Be_{1-x}B_x$ (x>0.11) coatings as deposited on stationary flat substrates is lost when thicker coatings are applied to bounced, hollow polymer capsules. This effect is attributed to large compressive stress that arise from the large B addition. As a second alternative, dopant impurities as Al, Fe, Ti, and Zr are well known to refine the grain size of Be.[2-5] In combination, the addition of B and Fe refines the Be microstructure to a grain size of only 10 nm and increases the measured hardness as well.[9] The possibility of producing a smooth (Be,B)-based ablator on polymer capsules is evidenced in the 1nm rms surface roughness measured for a 10 μm thick coating of $Be_{0.99-x}B_x(FeCrNi)_{0.01}$ sputter deposited onto a stationary capsule.

In addition to optimizing sputter deposition parameters and material composition, the source-to-substrate geometry is an important consideration. In a typical approach, the substrates randomly bounce and collide with one another in an ultrasonically-vibrated bounce pan. As an alternative to the open bounce pan method, an individual pocket chamber for each substrate (about twice the size of the mandrel diameter) is provided for coating.[9] The opening to each pocket chamber is designed to minimize glancing incident angles of deposition to further reduce roughness as well as to control heating from full exposure to the deposition source. It can be inferred from these findings that a microstructure on the nanoscale is essential to achieve strong and smooth Be-based coatings.

SUMMARY

Coatings of $Be_{1-x}Cu_x$ are prepared by magnetron sputter deposition. The application of a negative bias potential to the substrate induces ionized Ar bombardment during deposition that refines the columnar morphology and surface finish to the nanoscale. A tensile test is developed to load coated capsules under uniaxial tension. A -120 V applied bias produces an increase in strength from 25 MPa to 150 MPa for sputter deposited $Be_{0.98}Cu_{0.02}$ coatings. Concurrently, the surface roughness decreases from 0.15 μm to less than 50 nm. The bias-deposited material exhibits an increase in strength that follows a Hall-Petch type relationship with surface roughness.

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REFERENCES

1. S. Haan, Phys. Plasmas **2**, p. 2480 (1995).
2. R. Adams and C. Nordin, Thin Solid Films **181**, p. 375 (1989).
3. L. Tanner, and R. Ray, Acta Metall. **27**, p. 1727 (1979).
4. L. Tanner, Scripta Metall. **145**, p. 657 (1980).
5. C. Severin, C. Chen, A. Belova, and M. Lin, J. Appl. Phys. **52**, p. 1850 (1981).
6. Chen, C.W., and C.S. Alford, J. Vac. Sci. Technol., **A6**, p. 128 (1988).
7. R. McEachern, C. Alford, R. Cook, D. Makowiecki, and R. Wallace, Fusion Technology **31**, p. 4354 (1997).
8. R. McEachern and C. Alford, Fusion Technology **35**, p. 115 (1999).
9. A. Jankowski, P. Ramsey, M. McKernan and J. Morse, in *Amorphous and Nanostructured Carbon*, edited by J. Sullivan, J. Robertson, O. Zhou, T. Allen, and B, Coll, (Mater. Res. Soc. Proc. **593**, Pittsburgh, PA, 2000), pp. 489-492.

Biased Sputter Deposition of $Be_{1-x}Cu_x$ Coatings

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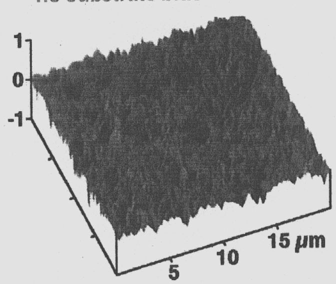
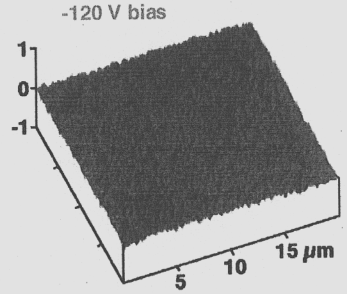
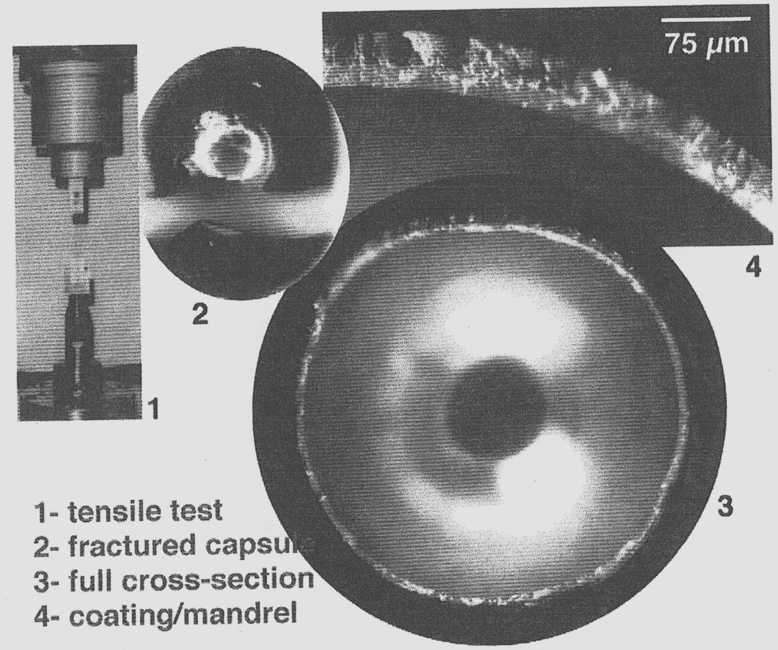
$Be_{1-x}Cu_x$ coatings are sputter deposited onto 1 mm dia, polymer mandrels that are mechanically bounced by ultrasonically driving a bowl-shaped, substrate pan. The application of a negative bias potential to the substrate pan induces ionized bombardment of the sputter gas during deposition, refining the columnar morphology and surface finish to the *nanoscale*. A tensile test is developed to load the coated capsules under uniaxial tension to failure at constant strain. A -120 V bias produces a three-fold increase in strength. Atomic force microscopy indicates a decrease in the surface roughness to less than 50 nm. These 7-10 µm thick $Be_{0.98}Cu_{0.02}$ coatings follow a Hall-Petch type relationship between strength and rms roughness.

no substrate bias



-120 V bias





1- tensile test
2- fractured capsule
3- full cross-section
4- coating/mandrel